ELIMINATION AND NEUTRALIZATION OF TOXIC SOIL SUBSTANCES.

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The fact that certain soils are naturally infertile, or if once fertile are showing a decrease in their productive power, is a subject that has engaged the attention of many able philosophers and scientists during the centuries. Some of these have explained the infertility as being caused by the absence or diminishing quantity of the store of certain mineral soil components, others have contended that the plant in its growth excreted waste substances, much as animals do, and that this toxic material poisoned succeeding crops, especially if they were of the same kind. The former of these views has led to the practice of supplying minerals in the form of fertilizers, the latter view, directly, or indirectly through dire necessity, to diversified farming or crop rotation. Thus both lines of reasoning lead to important practical results in maintaining and increasing the fertility of our agricultural lands, but neither view can as yet be said to have passed the controversial stage through which all great truths must pass.

I do not desire on this occasion to dwell on these two lines of reasoning but rather to present some new soil facts which would seem to coördinate the apparently opposite views and to modify both, so that each becomes at least broad enough to be tolerant of the other. I refer especially to the accumulating store of information gained through modern chemical and biological research, as to the nature of that portion of the soil components, variously designated as organic matter, soil humus, humic acid, matiere noire, etc., and the various biochemical changes which are taking place in soils, and ever giving rise to new compounds through decomposition or through synthesis, compounds which have distinct properties to influence plant growth or other biological activity in soils. With this knowledge comes the broader view that infertility in soils may as well be due to the presence of organic substances of biological origin inimical to proper plant development as to the absence of beneficial mineral elements. The existence of toxic organic compounds in soils has been amply shown by the researches of the Bureau of Soils into the nature of soil organic matter in infertile soils, and the properties of the isolated compounds in respect to their action on plants, so that the presence of toxic compounds in soils must be considered in connection with future work on the problems presented by infertile soils.

The scope of the investigation has necessarily been broader than a mere search for toxic substances and has included soil organic matter in general with the result that many organic compounds, both harmful and beneficial, have been found in the course of the investigation. With not a single soil compound isolated and identified a few years ago, those now definitely identified are as follows: Acrylic acid, adenine, agroceric acid, agrosterol, arginine, choline, creatinine, cytosine, dihydroxystearic acid, glycerides, guanine, hentriacontane, histidine, hypoxanthine, lignoceric acid, lysine, mannite, monohydroxystearic acid, nucleic acid, oxalic acid, paraffinic acid, pentosan, pentose, phytosterol, picoline carboxylic acid, resin, resin acids, resin esters, rhamnose, saccharic acid, salicylic aldehyde, succinic acid, trimethylamine, trithiobenzaldehyde, xanthine. A glance at the list will reveal the fact that most chemical classes are represented: hydrocarbons, acids and hydroxyacids, alcohols, aldehydes, esters, carbohydrates, hexone bases, purine bases, pyrimidine derivatives, sulphur compounds, etc. Most of them have been derived by biochemical changes taking place within the soil from the more complex compounds, from the fats, nucleoproteins, proteins, lecithins, etc. For instance, we may trace the complex nucleoprotein molecule through its various decompositions, first into protein and a complex nucleic acid which can further yield protein and nucleic acid. The protein resolves itself finally into such compounds as histidine, arginine, lysine, and possibly creatinine, all of which we have found in soils. The nucleic acid may split off phosphoric acid, or a carbohydrate such as the pentose mentioned above, and one or the other of the soil compounds, xanthine, hypoxanthine, guanine, adenine, or cytosine. This illustration serves to make clear the close relation existing between the biochemical changes which take place in the soil and those which take place in the animal. Of course the ultimate origin of all these soil compounds are to be found in the plant and animal debris which finds its way into the soil, through maturing plant parts, roots, animal excreta, dead animals, or added in agricultural practice in organic fertilizers, such as dried blood, tankage, or in green crops plowed under. In addition to these sources which are extraneous to the soil, there is the synthetic action of the microorganisms which inhabit the soil, but much further work needs to be done on these biochemical changes in soils before their entire course is understood. The forces which are operative we have already shown to be those of lysis in general, especially hydrolysis, oxidation, reduction, and catalysis. The life forms which produce these forces in the soil are the bacteria, molds, protozoa, yeasts, and the higher plants. All these contribute to the biochemical changes in soils either through the above forces operative as enzymes, or through the synthesis of the organic soil constituents from simpler organic and inorganic material.

After isolation and identification the soil compounds are studied in respect to their action on growing plants, wheat being usually used as an indicator. At the same time the action of various fertilizer salts in diminishing or accentuating the action of the soil compounds on plants is determined. In this manner much information concerning the physiological action of the compounds, together with suggestions for its neutralization or elimination are obtained. Owing to lack of material not all of the substances isolated have been studied in this comprehensive way, but sufficient information has been obtained to show that among the above enumerated compounds there are some that are distinctly toxic to plants, others that are distinctly beneficial and still others that are either doubtful or inert in so far as direct physiological effects are concerned.

Among the substances harmful to plants, picoline carboxylic acid, dihydroxystearic acid, oxalic acid, salicylic aldehyde and vanillin as having been found in unproductive soils should receive special mention. The first of these is only moderately toxic and has not been exhaustively studied, but is interesting in showing that nitrogen in such a compound is not only not available to plants, but that the compound containing it is unfavorable to plant development. The dihydroxystearic acid, on the other hand, has been more thoroughly studied and has been encountered in soils from many parts of the United States. It is a strong inhibitor of the normal processes of plant metabolism and destroys almost entirely the normal oxidizing power of plant roots, thus inhibiting root development and the power of absorption of mineral plant foods by the roots, even if present in the most available forms. Salicylic aldehyde is even more toxic than the dihydroxystearic acid and like salicylic acid it is a strong antiseptic, inhibiting the action of bacteria. This salicylic aldehyde was first discovered in a soil from the historic Mt. Vernon estate of George Washington, in the rose garden near the box hedge laid out by our first President. The remarkable fact in connection with this soil was that it contained a large amount of mannite, as much as 500 lbs. per acre. Although this is the only soil in which it has been found, the remarkable part was not in its being found there, for it can readily be produced by certain soil fungi, but rather that it should persist in the soil, when it is such an excellent medium for the development of bacteria. This sugar alcohol appeared to have no unfavorable effect on plants when it was tested in our greenhouse, but we were never able to make a good test because of the fact that the mannite solutions with the added fertilizer salts were such good media for the development of bacteria. The simultaneous presence of the salicylic aldehyde in the soil, and the fact that the latter was poisonous to higher plants, suggested therefore that the mannite in the soil was protected by the antiseptic action of the salicylic aldehyde. Experiments confirmed the antiseptic action of the salicylic aldehyde in preventing the decomposition of the above mannite solutions and the occurrence of the large quantity of mannite in this soil seems thereby explained. This case is particularly interesting as showing that soil compounds affect the lower life of the soil as well as the higher plant life, and through these the entire biochemical processes, and furthermore that even if a compound like mannite be not toxic in itself, its very presence points to the fact that the soil is functioning abnormally, much as the presence of sugar or albumen in the urine, in themselves harmless, point to the fact that something is decidedly abnormal with the metabolism of the individual excreting them. The occurrence of certain compounds in soils likewise becomes a great agent in the diagnosis of soil troubles. The occurrence of the dihydroxystearic acid is a not uncertain indication of low and sluggish oxidation in the soil, whatever may be the cause that has brought this about, be it poor drainage, acidity, poor physical management of the soil or other soil abuse.

The poisonous oxalic acid has been encountered in only one instance thus far, and that in a soil containing much calcium carbonate. The amount, however, was so extremely large, nearly four tons of calcium oxalate per acre, that it is thought to play some part, even as the insoluble oxalate, in the peculiar failure of apple orchards in this soil. Experiments in greenhouse and orchard are still under way to determine these facts and I mention this case here only to point out the application of this type of investigation to problems where other means fail to diagnose the trouble. Another application of such work is in diagnosing the soil trouble which brings about the mysterious disease of the orange tree and fruit known as dieback with which growers have struggled for years with annual loss of thousands of dollars and which scientists now consider as a physiological disease, that is, one not caused by any pathological organisms extraneous to the plant itself. All facts point to the soil condition as the cause, but so inexplicable has been its behavior in respect to the soil that all ordinary means of chemical investigation have failed to lay bare the cause or causes. Typical dieback soils from Florida are now under investigation in our laboratories at Washington to determine in them such organic constituents as are possible by the methods so far developed. This work is meeting with success and a number of compounds have been isolated and these will be studied in regard to their effect on orange trees in coöperation with Professor Floyd, of the Florida Experiment Station, to see whether they are responsible for this disease. Like the apple orchard experiment this work is still in progress and not sufficiently well advanced to discuss its practical significance but it serves to show the application of this type of biochemical investigation to certain great economic problems which confront many agricultural industries. Another of these harmful soil constituents is the pleasant smelling vanillin, a constituent of the vanilla bean, but also of many other plants, as shown in this and many other laboratories, and a compound which is somewhat harmful to wheat seedlings in solution cultures, chemically an aldehyde and thus a reducing agent capable of being oxidized and having its harmful properties reduced by such oxidizing fertilizers as nitrates. The properties of vanillin in regard to plant growth and its effect on root oxidation and the influence of fertilizer salts on its action, were determined on wheat in our laboratories several years ago in anticipation of the day when it would be found as a soil constituent. What is true in this respect of vanillin is also true of a number of other compounds but it is also equally true that some of the soil constituents isolated were not even remotely suspected of ever being found in soils, and in fact some of them have been previously only known as products of the chemist's laboratory, for instance, the saccharic acid, a laboratory oxidation product of sugars, or the trithiobenzaldehyde, previously only known as a sulphur substitution product of the laboratory.

While the subject of my talk limits me chiefly to a discussion of the soil substances which we have found to be harmful in our experiments, I must not omit in passing to speak of the many beneficial substances which have been discovered in soils as the result of these investigations, and which even more than the toxic substances, make clear the parallelism existing between the biochemistry of the soil and the biochemistry of the animal, because some of the compounds involved are absolutely identical. Among this list of beneficial soil compounds you will recognize common products of animal metabolism and digestive processes such as creatinine, found in the urine; histidine, arginine, lysine, products of protein digestion; xanthine, hypoxanthine, products of animal fluids and nuclein degradation; and nucleic acid itself. These compounds increase plant growth and the results obtained would seem to show that the plant can use these compounds directly in building up the plant proteins and nucleins without further decomposition to ammonia and production of nitrites and nitrates.

Nor should I pass over the physiologically doubtful or inert soil substances without suggesting that these have a potentiality for good or bad, depending upon future changes brought about by oxidation, reduction, or other biochemical action resulting in the production of beneficial or harmful compounds. Nor should I fail to mention that many of these physiologically inert substances, as, for instance, the water insoluble resins, have a marked physical effect on the soil, often coating the soil grains and shielding the soil minerals as well as other organic substances from the solvent action of the soil waters, thus effectively interfering with an otherwise normal soil.

In speaking of the elimination and neutralization of toxic soil substances we must not lose sight of the fact now fairly well demonstrated by biochemical and biological researches that in every soil there is a balance of beneficial and harmful factors, soil fertility or infertility being the resultant of the two groups. As one or the other group of factors gains the ascendency, the fertility is raised or lowered, as the case may be. This balance is influenced by cultural treatment, such as draining, plowing, or otherwise working the soil, by the application of fertilizers, by liming, by the growth of plants, by crop rotation, etc. All of these factors affect the biology of the soil, the soil bacteria, the molds, and other microörganisms and through them the entire biochemical process in soils. Although the number of toxic soil constituents may be very large and probably but imperfectly represented by those we have thus far been able to isolate, it appears nevertheless significant that they are substances which have resulted from partial oxidation, but in their present form have reducing properties, and under favorable conditions are subject to further oxidation. They may be said to have resulted under imperfect conditions of oxidation or aeration whether this be the direct result of poor drainage, of soil acidity, or lack of lime, or poor cultivation, or the growth of crops which do not promote deep root growth or active root oxidation. The studies which we have made on soils in respect to their ability to oxidize organic substances such as aloin has shown us that fertile soils are generally good oxidizers and infertile soils poor oxidizers. In soils that are good oxidizers the chances of having an undue accumulation or even formation of toxic substances are at a minimum, whereas in poor soils with low oxidizing power, with low vitality as it were to properly digest the organic refuse of previous growth, harmful substances result. The chief aim in improving unfertile soils should therefore be to build them up so that they will become good oxidizers and through this become strong virile soils. In the laboratory and greenhouse we have been able to observe the disappearance of toxic soil conditions by thorough aeration and exposure to air, by the action of lime, and by the influence exerted by fertilizers, especially the oxidizing fertilizers like sodium nitrate, or the catalytic influence of oxidizing substances like manganese. In the field the most useful agents are (1) better drainage, which promotes better aeration and increases the oxidation in the soil; (2) liming, which in addition to neutralizing acid tendencies, or combining with the substances to form insoluble or inert compounds, has also the effect of increasing the oxidation in the soil and in the plant roots as well as to have a physiological effect on the plant cells themselves which makes them more resistant to poisons in general; (3) crop rotation, which gives to the soil each year a different kind of organic debris, changing as it were, the normal food of the soil, from time to time, and furthermore necessitates different cultural methods and different fertilization systems, alternating cultivated crops with uncultivated crops, shallow rooted plants with deep rooted plants, grain crops with root crops, leguminous with non-leguminous crops, with the result that the biochemical changes in the soil, the digestion, the oxidation, the catalysis, of the soil, proceeds in a normal manner, the balance of soil factors being influenced in a favorable direction and a healthy normal soil results; and (4) fertilization, which is usually done with the motive of adding plant food, but which the more modern investigations in biological and biochemical fields are showing to be an accessory to proper soil treatment because in addition to supplying needed plant nutrients they influence the microörganic life within the soil, because they influence the oxidation in the soil, the catalysis in the soil, the digestive processes in the soil, so that the biochemical processes are altered, the balance of factors influencing plant growth is changed, because they influence the oxidation of plant roots, and because, directly or indirectly, they effect the destruction, the neutralization, or prevent the formation of harmful substances. I have not considered here the mechanical composition of the soil particles, the big natural agencies which have operated to form soils, the location or topagraphy of the lands and the normal water capacity of soils, the origin of soils, or their relation to climate and rainfall, all of which factors influence soil type and contribute to make some soils naturally more fertile than others, naturally adapted for the growth, and sometimes the continuous growth of one crop, while unsuited to another, facts which must receive more and more attention in the future if we are to get the maximum returns from our soils. I am considering only the means which will tend to maintain or increase the fertility to a status normal to that kind of soil, to maintain it in a healthful, virile state.

The great question before scientific agriculture is not whether fertilizers are helpful, no more than modern medical science considers whether foods or medicines are helpful, but rather how can these be made more efficient, more certain in their action, more specific in their application to the needs of the soil. Soil students have in the past century contented themselves practically with a single factor of soil infertility, a not unimportant factor it must be admitted, but nevertheless one insufficient to explain all difficulties, namely, that of plant starvation, the question of lacking plant food. The studies have centered about the food of the plant while the surroundings, the home of the plant, the soil itself, has been virtually ignored, or given only minor consideration, except as a storehouse for plant food. Even in the more scientific work of the past decade in reference to bacteria, and other biological work, the production of plant food has been the motive of all study and all discussion is from the point of view of liberating potash, phosphate, or increasing the quantity of nitrogen for the use of the plant. The biochemistry of these life forms in the soil, the multitudinous changes which they work have remained unstudied, only those facts were determined which influence the amount of the so-called plant food, ignoring even much material that is more truly plant food than the mineral substances and inorganic nitrogen compounds studied. In all lines of human activity the sanitary surroundings, the proper medical treatment and the proper nutrition of animals and of man, are receiving attention and the proper sanitary condition of the plant's home, the soil, will also receive more and more attention to prevent its harboring the germs of devastating plant diseases, and such decompositions or biochemical changes as produce substances inimical to the health of the plant, killing it or weakening it, so that it falls a ready prey to pathological organisms. In this campaign for a sanitary home for the plant, the above factors of better cultivation, better drainage, judicious liming, crop adaptation or crop rotation, and the use of fertilizers, will play an important part and as we learn more of the functions of the latter, their use will become more general and more specific so that we will be able to tell which will be the best suited for any particular soil condition or soil trouble, and in the future these will no doubt be modified and even augmented with other chemicals to meet special requirements. Some such special fertilizers are already on the market and more will follow, the only danger is that the advertising art will outstrip the science, which should be the basis for such changes.

The use of copper preparations in special orange fertilizers, or the use of manganese or other catalytic substances to promote oxidation in soils are illustrations of such use. The oxidation by manganese has received special attention in our laboratories and in the field and the conclusion seems warranted that such catalytic substances depend upon the form in which they are introduced or present in the soil and the form of the organic matter in the soil, which with the manganese forms activating combinations. In the field work its action is still uncertain so far as increased oxidation or increased crop growth is concerned. On poor soils, with acid tendencies, the results are doubtful, as will be shown by a forthcoming bulletin on the field experiments over a period of five years on such an acid soil. A second period in which the soil will be limed to produce neutrality is now begun and it will be interesting to learn how the manganese will behave under this new condition.

That even the ordinary chemicals used in fertilizers, potash, phosphates, or nitrates can affect the harmful action of organic substances has already been incidentally alluded to in the preceding paragraphs. Our researches have shown that the harmful soil constituents, vanillin and dihydroxystearic acid have their poisonous effects greatly diminished or even entirely overcome by the addition of sodium nitrate, whereas their harmful characteristics remain unimpaired by the addition of phosphates or potash fertilizers. Nitrate is an oxidizing substance and we have shown root oxidation to be increased greatly by its use, whereas both vanillin and dihydroxystearic acid decrease root oxidation and are themselves capable of being oxidized. The effect of nitrate and these two substances are therefore opposed to each other and thus neutralize each other, or, what is more probable, neutralize their effects. The substance, quinone, on the other hand has its poisonous action reduced by potash salts, not by nitrate nor phosphate. Quinone is an active oxidizing substance, while potash reduces root oxidation thus again showing that these two substances antagonize each other in their effects. The substance cumarin we have found to be very toxic to plants. This toxicity is not diminished by nitrate nor by potash, as was the case respectively with the preceding substances, but its action was most remarkably overcome by the addition of phosphate and it seemed to make no difference in what form the phosphate was used, whether it was as a calcium salt or as a sodium salt, or as the monobasic, dibasic, or tribasic salt.

I have mentioned these illustrations of specific fertilizer action to show the possibilities of the future in adapting fertilizer treatment to meet the specific needs of the soil based upon a perfectly rational basis of soil treatment to meet the requirements of specific crops or the requirements of plants suffering from unhealthy, insanitary soil conditions, which involve the presence of biochemical transformations resulting in compounds detrimental to the best plant development.